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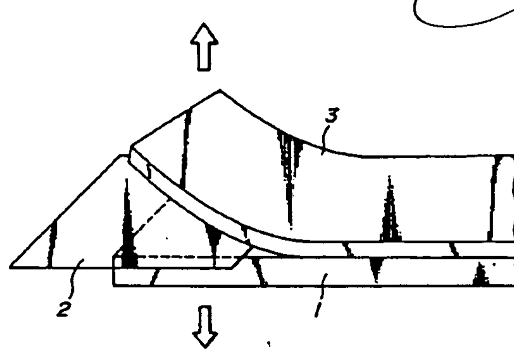
(54) Rubber composition.

(57) A rubber composition includes a rubber component and particulates of a crystalline syndiotactic-1,2-polybutadiene resin dispersed therein. The particulates have an average particle diameter of 1 to 500 μm, and the melting point of the crystalline syndiotactic-1,2-polybutadiene resin is not less than 110°C. The compounding ratio of the resin is 5 to 60 parts by weight relative to 100 parts by weight of the rubber component. The rubber composition is particularly useful for tires, and other rubber articles.

FIG_1



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The present invention relates to a rubber composition having a large slip friction resistance and a small specific gravity, whil fracture resistance or wear resistance are not lost.

With respect to tires as well as other rubber articles, needs have been recently increasing for rubb r materials having large slip friction resistance under various use conditions with ut losing fracture resistance or a wear resistance conventionally possessed.

On the other hand, needs have been increasing for lightening rubber articles from the standpoint of terrestrial environmental conservation.

For such needs, for example, the slip friction resistance is increased by using a styrene-butadiene rubber having a large tan δ and obtained by emulsion polymerization, increasing a charged amount of carbon black and adding a great amount of oil in view of appropriate rubber hardness and practical processability. However, the slip friction resistance currently required cannot be fully obtained by the above compounding conditions. Further, an amount of heat generated inside the rubbet article increases under dynamic use conditions to conspicuously lower durability due to degradation of rubber, and the specific gravity of the rubbet article becomes greater.

Besides the above method, solution-polymerized styrene-butadiene rubbers have been recently investigated in various ways, and there have been proposed methods of using a solution-polymerized styrene-butadiene rubbet having a specific molecular structute or compounding specific fibers or filler into a rubber.

However, although the slip friction resistance can be considerably improved on ordinary roads by specifying the molecular structure of the polymer to be employed, satisfactory slip friction resistance cannot be obtained on ice.

Further, when the special fibers or filler is compounded into rubber, good effect on the slip friction resistance can be obtained even on ice. However, since the fibers or filler added acts as a foreign material in the rubbet, fracture resistance or wear resistance is remarkably deteriorated.

As mentioned above, it is a present situation that a rubber composition having a large slip friction resistance on roads in any state and a small specific gravity without losing fracture resistance or wear resistance have not yet been obtained.

It is an object of the present invention to provide a rubber composition having a large slip friction resistance on roads in any state and also a small specific gravity without losing fracture resistance or wear resistance.

Inventors' investigations have revealed that even when interface bonds are formed between rubbet and a special particulate compounding chemical incorporated into the rubber composition, the thus formed interface bonds are not necessarily sufficient if dynamic external deformation is intermittently inputted, for example, in the case of tires.

The inventors have made further investigations to form effective interface bonds between rubber and the particulate material, and found that the above problems can be solved by forming a co-crosslinked structure between the added particulate material and rubber. Based on this discovery, the present inventors have accomplished the present invention.

That is, the rubber composition according to the present invention includes a rubber component and particulates of a crystalline syndiotactic-1,2-polybutadiene resin, wherein the average particle diameter of the resin is 1 to 500 μm, the melting point of the resin is not less than 110°C, and the compounding ratio of the resin is 5 to 60 parts by weight relative to 100 parts by weight of the rubber component.

The particulates of syndiotactic-1,2-polybutadiene resin used in the present invention need to have the average particle diameter of 1 to 500 μm. If the average particle diameter is less than 1 μm, slip friction resistance aimed at by the present invention cannot be sufficiently improved. On the other hand, if the average particle diameter is more than 500 μm, fracture resistance and wear resistance are unfavorably deteriorated. The average particle diameter of the particulate resin used in the present invention is preferably 8 μm-480 μm, and mote preferably 100 μm-480 μm.

The syndiotactic-1,2-polybutadiene resin used in the present invention needs to be in the particulate form. The average ratio M between the major axis and the minor axis of the resin particulates is preferably not more than 6, more preferably not more than 4, in the state that the resin is kneaded into the rubber composition. If the resin is used in the form of micron pile fibers, the resin is oriented during processing the rubber mixture, for example, rolling or extruding, so that enlargement of coefficient of friction aimed at by the present invention unfavorably depends upon the direction.

Further, such particulates of the syndiotactic-1,2-polybutadiene resin need to have the melting point of not less than 110°C. The melting point of the particulate resin is preferably 115°C-200°C, and more preferably 120°C-195°C. The syndiotactic-1,2-polybutadien resin having the melting point of less than 110°C is n t preferable, because its crystallinity is l w and hardn ss f the particulates th ms lves is small. Further, since such particulates are softened or deform d due to internal heat g neration under dynamic us conditions, slip friction resistance cannot be improved as desired.

If the ratio of the abov syndiotactic-1,2-polybutadien resin is less than 5 parts by weight relative to 100 parts by weight of the rubber component in the rubber composition, improvement on the slip friction resistance of the resulting rubber article cann t almost b recognized, and contributi n to reduction in the sp cific gravity is small. On the other hand, if th ratio of the syndiotactic-1,2-polybutadien resin is more than 60%, slip friction resistance of th resulting rubber article is improved with reduced sp cific gravity, whereas fracture resistance and wear resistance of the rubber article are not only largely deteriorated but also processability of the rubber composition is conspicuously deteriorated to make the rubber composition practically unsuitable.

The above syndiotactic-1,2-polybutadiene can be produced according to a process disclosed in Japanese patent publication No. 53-39,917, 54-5,438 or 56-18,005. However, the process of producing the syndiotactic-1,2-polybutadiene used in the present invention is not limited to those in these publication.

In the present invention, the kind of the rubber constituting the rubber composition in which the composite particulates of the syndiotactic-1,2-polybutadiene resin are incorporated needs not necessarily be limited to any specific ones, and ordinarily used rubber may be employed. For example, as the rubber component, natural rubber, polyisoprene rubber, polybutadiene rubber, styrene-butadiene copolymer rubber, butyl rubber, halogenated butyl rubber, and ethylene-propylene diene rubber may be preferably used singly or in combination with each other.

Needless to say, a compounding agent ordinarily used in the rubber industry, for example, other polymer, carbon black, vulcanizer, vulcanizing accelerator, etc. may be compounded into the rubber composition according to the present invention in appropriate amounts.

Since the highly crystalline syndiotactic-1,2-polybutadiene resin is dispersed in the rubber composition according to the present invention, the rubber composition has a structure having the hard particulate material exposed to the surface of the rubber composition. Thus, excellent slip friction resistance can be attained even on wet roads and ice roads.

The syndiotactic-1,2-polybutadiene resin forms a tough crosslinked structure between rubber through vulcanization or the like. Therefore, even when the rubber composition according to the present invention is used for the rubber article, such as tire, to which dynamic external deformation is intermittently applied, the particulates will not almost be peeled or slip off from the rubbet as matrix, contrary to the conventional rubber compositions. Consequently, fracture resistance and wear resistance are largely improved.

These and other objects, features and advantages of the present invention will be appreciated upon reading of the following description of the invention when taken in conjunction with the attached drawing, with the understanding that some modifications, variations and changes of the same could be made by the skilled person in the art to which the invention pertains without departing from the spirit of the invention or the scope of claims.

For a better understanding of the invention, reference is made to the attached drawing, wherein:

Fig. 1 is a view illustrating a peeling test for examining the co-crosslinkability between rubber and resin.

The present invention will be explained in more detail with reference to examples and comparative examples.

First, methods for measuring various physical properties of the examples and comparative examples will be explained.

(1) Melting point of syndiotactic-1,2-polybutadiene resin:

The resin was heated at a heating rate of 10°C/min in a temperature range from 30°C to 250°C, and an endothermic peak was obtained by using a differential thermal analyzer DSC 200 manufactured by SEIKO ELECTRONICS CO., LTD. The melting point of the resin was detetmined based on the thus obtained endothermic peak.

(2) Slip friction resistance:

① Dry skid resistance

Tan δ of a vulcanized rubber composition was measured at 30°C and a frequency of 10 Hz by using a spectrometer manufactured by IWAMOTO SEISAKUSHO CO., LTD. Results are indicated by index. The greater the index, the better is the dry skid resistance.

② Wet skid resistance

Skid resistance on wet road (wet skid resistance) of the rubber composition was measured at room temperature by using a skid resistance meter manufactured by STANLEY CO., LTD. Results are indicated by index. The greater the index, the better is the wet skid resistance.

③ Ice skid resistance

The coefficient of friction on ice of the rubber composition, particularly the coefficient of friction on ice near 0°C in a wet state, was measured with use of a dynamic-static fricti n co fficient meter manufactured by KYOWA KAIMEN KAGAKU, CO., LTD. by contacting a surface of a sampl (sampl dimensions: 10 mm long, 10 mm wide and 5 mm thick) obtained from a slab sheet produced by rdinary vulcanizati n with ice having a surface t mperature f -0.5°C.

Th measuring conditions were a load of 5 kgf/cm^2, a sliding speed of 10 mm/sec, a surrounding temperature of -2°C, and the ice surface state being substantially a mirror.

(3) Fracture resistance:

Fracture resistance of the rubber composition was measured according to JIS K 6301, and results are indicated as t nsile strength by index. The greater the index, the better is the fracture resistanc .

(4) Wear resistance:

Wear resistance of the rubber composition was measured by a Lambourn abrasion tester manufactured by IWAMOTO SEISAKUSHO CO., LTD. Results are indicated by index. The greater the index, the better is the wear resistance.

(5) Specific gravity:

The specific gravity of the rubber composition was measured by using an automatic densitometer (AUTOMATIC DENSIMETER) manufactured by TOYO SEIKI CO., LTD.

Next, the process for producing the syndiotactic-1,2-polybutadiene resin used in the present Examples will be explained.

Dewatered benzene, 760 cc, was charged into a 2-liter autoclave in which air was replaced by nitrogen gas, and 74 g of 1,3-butadiene was dissolved into benzene. To the solution was added 1 m mol cobalt octoate (a benzene solution containing 1 m mol/cc of cobalt octoate), and 1 minute thereafter 2 m mol triethyl aluminum (benzene solution containing 1 m mol/cc triethyl aluminum) was added and stirred. One minute later, acetone was added in an amount shown in Table 1. Further, one minute later, carbon dioxide, 0.6 m mol (benzene solution containing 0.3 m mol/cc) was added into the mixture, which was stirred at 10°C for 60 minutes to effect polymerization of 1,3-butadiene.

2,4-Ditertial-butyl-p-cresol, 0.75 g, was added to the syndiotactic-1,2-polybutadiene resin-produced liquid. Then, the resulting liquid was added into 1,000 cc of methanol, thereby precipitating syndiotactic-1,2-polybutadiene resin.

The thus obtained syndiotactic-1,2-polybutadiene resin was further washed with methanol, and methanol was filtered off, followed by vacuum drying.

Table 1

Kind of resin	A	B	C	D	E	F
Addition amount of acetone (m mol)	2200	1100	290	5	7000	3700
Melting point (°C)	121	140	170	194	87	106

Next, occurrence of the co-crosslinked structure between the thus produced syndiotactic-1,2-polybutadiene resin and rubber was judged by the following method.

As shown in Fig. 1, an about 1 mm thick sheet of the syndiotactic-1,2-polybutadiene resin or nylon-6 and an about 1 mm thick unvulcanized rubber sheet obtained by kneading a rubber composition having a compounding recipe shown in Table 2 (parts by weight) were attached together through a cellophane film 2 at opposite end portions thereof, and the obtained thick sheet having a total thickness of 2 mm was subjected to vulcanization under given vulcanization conditions in a press mold.

Then, the vulcanized sheet was cut in a width of 1 cm, and subjected to a peeling test at a peeling speed of 20 mm/min as shown in Fig. 1. Results in the peeling test were judged in the following criterion.

Not co-crosslinked ··· No rubber 3 was attached to the resin 1 in Fig. 1 (interface peeling).

Co-crosslinked ··· Rubber 3 was clearly attached to the resin 1 (cohesion peeling).

Results are shown in Table 3.

Tabl 2

	Parts by weight
Natural rubber	100
Carbon black N339	45
Stearic acid	1.0
Zinc oxide	2.0
Antioxidant vulcanization accelerator	1.0
Sulfur	1.5

Table 3

Resin (melting point of crystal °C)	Syndiotactic-1,2-polybutadiene resin			Nylon-6
	(130)	(140)	(160)	
Attachment of rubber to resin	attached	attached	attached	not attached

(Note) Vulcanizating conditions: 145°C, 30 min.

As is seen from Table 3, it is clear that when the syndiotactic-1,2-polybutadiene resin was incorporated into the rubber composition as the particulate material and the composition was vulcanized by the ordinary method, the co-crosslinked structute was formed at the interface between the rubber component as the matrix and the particulate material. Therefore, as compared with the particulate nylon-6 material having formed no co-crosslinked structure, it is understood that the syndiotactic-1,2-polybutadiene resin improves fracture strength. It can be expected that the following wear resistance is also enhanced by the improvement on the fracture strength.

Examples 1-4 and Comparative Examples 1-3

The average particle diameter of each of the syndiotactic-1,2-polybutadiene resins, A, B, C, D, E and F shown in Table 1 was adjusted to 150 μm by an ordinary method. The average particle diameter was measured by an air jet sieve grain size 200 LS type meter manufactured by ALPINE CO., LTD. The obtained syndiotactic-1,2-polybutadiene resin was compounded according to a compounding recipe (parts by weight) shown in Table 4 to obtain a vulcanizate. Physical properties of the vulcanizate are also shown in Table 4.

Table 4

		Comparative Example 1	Example 1	Example 2	Example 3	Example 4	Comparative Example 2	Comparativ Example 3
Natural rubber		50	50	50	50	50	50	50
Butadiene rubber		50	50	50	50	50	50	50
Carbon black N339		50	50	50	50	50	50	50
Process oil		5	5	5	5	5	5	5
Stearic acid		1.0	1.0	1.0	1.0	1.0	1.0	1.0
ZnO		3.0	3.0	3.0	3.0	3.0	3.0	3.0
Antioxidant		1.0	1.0	1.0	1.0	1.0	1.0	1.0
Vulcanization accelerator		1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur		1.5	1.5	1.5	1.5	1.5	1.5	1.5
Syndiotactic-1,2-polybutadien resin	A	-	20	-	-	-	-	-
	B	-	-	20	-	-	-	-
	C	-	-	-	20	-	-	-
	D	-	-	-	-	20	-	-
	E	-	-	-	-	-	20	-
	F	-	-	-	-	-	-	20
Dry skid resistance		100	100	101	102	100	105	102
Wet skid resistance		100	101	105	108	100	95	98
Ice skid resistance		100	170	190	221	253	98	101
Tensile strength (Index)		100	107	101	95	89	99	105
Wear resistance (Index)		100	121	118	101	98	103	99
Specific gravity		1.11	1.08	1.06	1.07	1.07	1.07	1.08

Examples 5-8 and Comparative Examples 4-6

The average particle diameter of th syndiotactic-1,2-polybutadiene resin B shown in Table 1 was adjusted to a value shown in Table 5 by controlling a milling time in th ordinary m thod.

Table 5

	B-1	B-2	B-3	B-4	B-5	B-6
Average particle diameter (μm)	0.5	10	148	243	460	530

Each of the syndiotactic-1,2-polybutadiene resins shown in Table 5 was compounded according to a compounding recipe shown in Table 6 (parts by weight) to obtain a vulcanizate. Physical properties of the resulting vulcanizate are also shown in Table 6.

Table 6

	Comparative Example 4	Comparative Example 5	Example 5	Example 6	Example 7	Example 8	Comparative Exampl 6
Natural rubber	100	100	100	100	100	100	100
Carbon black N110	45	45	45	45	45	45	45
Process oil	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2
ZnO	3	3	3	3	3	3	3
Antioxidant	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Vulcanization accelerator	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Syndiotactic-1,2-polybutadien resin B-1	-	20	-	-	-	-	-
B-2	-	-	20	-	-	-	-
B-3	-	-	-	20	-	-	-
B-4	-	-	-	-	20	-	-
B-5	-	-	-	-	-	20	-
B-6	-	-	-	-	-	-	20
Dry skid resistance	100	101	98	102	100	99	96
Wet skid resistance	100	98	101	104	103	107	110
Ice skid resistance	100	95	105	247	181	155	123
Tensile strength (Index)	100	110	103	97	98	91	78
Wear resistance (Index)	100	104	103	100	98	96	85

Examples 9-11 and Comparativ Examples 7-9

Th syndiotactic-1,2-polybutadi ne resin (B-3) sh wn in Table 5 was used, and compounded according to a compounding recipe shown in Table 7 (parts by weight) to obtain a vulcanizate. Physical properties of the resulting vulcanizat ate also sh wn in Tabl 7.

Table 7

	Comparative Example 7	Comparative Example 8	Example 9	Example 10	Example 11	Comparative Example 9
Natural rubber	70	70	70	70	70	70
Butadiene rubber	30	30	30	30	30	30
Carbon black N220	55	55	55	55	55	55
Process oil	7	7	7	7	7	7
Stearic acid	2	2	2	2	2	2
ZnO	3	3	3	3	3	3
Antioxidant	1.5	1.5	1.5	1.5	1.5	1.5
Vulcanization accelerator	1.5	1.5	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5	1.5	1.5
Syndiotactic-1,2-polybutadiene resin B-3	-	3	10	30	50	90
Dry skid resistance	100	95	98	102	100	90
Wet skid resistance	100	90	104	105	108	98
Ice skid resistance	100	97	115	263	173	109
Tensile strength (index)	100	103	105	99	95	76
Specific gravity	1.12	1.11	1.09	1.06	1.06	1.03
Kneadability *)	○	○	○	○	○	x

Note: Evaluation standard for kneadability is as follows:

○ ··· Kneaded mixture could take an integral sheet-like form on a roll, and could be post-processed.

x ··· Kneaded mixture could not take an integral form on the roll, and could not be post-processed.

As is clear from the above-mention d test results, according to th rubber composition of th present invention, the particulates of the syndiotactic-1,2-polybutadiene resin having the average particle diameter and

the melting point as specified abov is incorporated into the rubber composition at the specified compounding ratio. Thus, conspicuous improvement n th slip friction resistance can be recognized without losing fracture resistance and wear resistance. Further, since th rubb t composition according to th present invention has a small specific gravity, the above effects are extremely great.

Claims

1. A rubber composition comprising a rubber component and particulates of a crystalline syndiotactic-1,2-polybutadiene resin, said particulates having an average particle diameter of 1 to 500 μm and the melting point of said crystalline syndiotactic-1,2-polybutadiene resin being not less than 110°C, and the compounding ratio of the said resin being 5 to 60 parts by weight relative to 100 parts by weight of said rubber component.

2. A rubber composition as claimed in claim 1, characterized in that an average ratio between a major axis and a minor axis of the particulates of the resin is not more than 6.

3. A rubber composition as claimed in claim 1 or 2, characterized in that the melting point of the crystalline resin is 115°C to 200°C.

4. A rubber composition as claimed in claim 3, characterized in that the melting point of the crystalline resin is 120°C to 195°C.

5. A rubber composition as claimed in any of claims 1 to 4, characterized in that the average particle diameter of the particulates is 8 μm to 480 μm.

6. A rubber composition as claimed in claim 5, characterized in that the average particle diameter of the particulates is 100 μm to 480 μm.

7. A rubber composition as claimed in any of claims 1 to 6, characterized in that the rubber component is at least one rubber selected from natural rubber, polyisoprene rubber, polybutadiene rubber, styrene-butadiene copolymer rubber, butyl rubber, halogenated butyl rubber, and ethylene-propylene diene rubber.

FIG_1